#1	#2	#3	#4	Total	Bonus
15	15	15	15	60	6

Midterm Assessment #2 (60 pts)   **Chem 20B, Winter 2017**

March 7th, 2016 (5:30 - 7:00 pm)

Only non-programmable, scientific calculators are allowed. The use of graphing calculators, cell phones, personal computers, and any other electronic device is strictly forbidden. Read the entirety of the questions carefully before you begin answering them. If a question asks you to determine a numerical value, you must include **appropriate units** and a reasonable number of significant figures. STATE ANY ASSUMPTIONS YOU MAKE AND SHOW ALL OF YOUR WORK. In some cases, a well-reasoned, written argument may be substituted for some mathematical work. If you run out of space on the front of the page, use the back of the page and indicate on the front of the page that your work continues the back.

Constants and Conversions

$N_A = 6.022 \times 10^{23}$

$1 \text{ kg} = 10^3 \text{g}$

$R = 0.08206 \text{ L atm mol}^{-1} \text{ K}^{-1} = 8.314 \text{ J mol}^{-1} \text{ K}^{-1}$

$1 \text{ atm} = 101325 \text{ Pa} = 760 \text{ mmHg} = 760 \text{ torr}$

$1 \text{ L} = 10^3 \text{mL} = 10^{-3} \text{ m}^3$

$0°C = 273.15 \text{ K}$

$K_w = 10^{-14}$ at 25°C

$k_B = 1.38 \times 10^{-23} \text{J/molK}$

Normal temperature: 298K

Quadratic formula

$$x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}$$

Equations

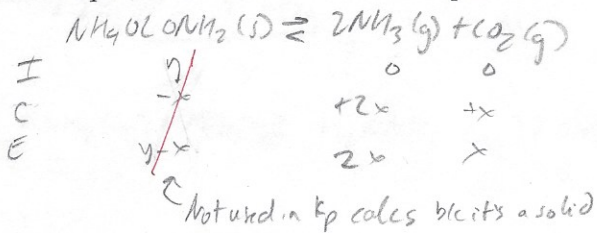|		
$PV = nRT$	$S = k_B \ln \Omega$	$\text{molarity} = \dfrac{n_{\text{solute}}}{L_{\text{solution}}}$
$P_{Total} = P_A + P_B + P_C + \cdots$	$\Delta S = nC_p \ln \dfrac{T_f}{T_i}$	$\Delta H_{rxn} = \sum n_p \Delta H_f(\text{products}) - \sum n_r \Delta H_f(\text{reactants})$ $\Delta H = \Delta H_1 + \Delta H_2 + \Delta H_3 + \cdots$
$\Delta U = q + w$	$\Delta S = nR \ln \dfrac{V_f}{V_i}$	$\Delta G = \Delta H - T\Delta S$
$q_v = nC_v\Delta T$	$\Delta S = \dfrac{\Delta H_\phi}{T_\phi}$	$\Delta G° = -RT \ln K$
$q_p = nC_p\Delta T$	$\dfrac{(P_C)^c(P_D)^d}{(P_A)^a(P_B)^b} = K$	$\dfrac{[C]^c[D]^d}{[A]^a[B]^b} = K$
$w = -P_{ext}\Delta V$	$\text{pH} = -\log[H_3O^+]$	$[H_3O^+] = 10^{-pH}$
$\Delta U = nC_v\Delta T$	$\text{pOH} = -\log[OH^-]$	$\text{pH} + \text{pOH} = 14$
$\Delta H = nC_p\Delta T$	$K_a = \dfrac{[H_3O^+][A^-]}{[HA]}$	$pK_a = -\log K_a$
$C_p = C_v + R$	$K_b = \dfrac{[OH^-][BH^+]}{[B]}$	$pK_b = -\log K_b$
$\Delta H = \Delta U + \Delta(PV)$	$K_a = 10^{-pK_a}$	$K_b = 10^{-pK_b}$

PLEASE "BOX" YOUR FINAL CALCULATED VALUES AND INDICATE WHICH VARIABLES
THEY REFER TO.

1) (15 pts) Ammonium carbamate is the ammonium salt of carbamic acid. It is used as a nitrogen fertilizer and in the manufacture of urea. At 25 °C, it decomposes by the following process:

$$NH_4OCONH_2 \ (s) \leftrightharpoons 2\ NH_3\ (g) + CO_2\ (g) \qquad\qquad K_p = 2.9\times10^{-3}$$
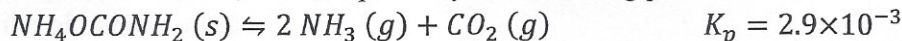
A sample of ammonium carbamate is placed in a sealed, rigid container with a volume of 1 L and allowed to come to equilibrium.

a. What is the total pressure in the container at equilibrium?

$$NH_4OCONH_2 \ (s) \rightleftharpoons 2NH_3 \ (g) + CO_2 \ (g)$$

I   η   0   0
C   -x   +2x   +x
E   y/x   2x   x

← Not used in K_p calcs b/c its a solid

$$K_p = (P_{NH_3})^2 \ (P_{CO_2})$$

$$P_T = \frac{nRT}{V}$$

$$= \frac{(3 mol)(0.082 \ L atm)(298 K)}{mol \cdot K}$$
$$\qquad\qquad 1 L$$
$$= 73.4 \ atm$$

$$2.9\times10^{-3} = (2x)^2 (x)$$

$$\frac{2.9\times10^{-3}}{4} = x^3$$

$$x = 8.98 \times10^{-2} \ atm$$

$$\approx 9.0 \times10^{-2} \ atm \ (sig \ figs)$$

$$P_{NH_3} = 2x = 2(9.0\times10^{-2} \ atm) = 0.18 \ atm$$

$$P_{CO_2} = x = 0.090 \ atm$$

$$P_{Total} = P_{NH_3} + P_{CO_2} = 0.18 \ atm + 0.090 \ atm = \boxed{0.27 \ atm}$$

+12

b. If the sample of ammonium carbamate was instead placed in a container with a volume of 3 L and allowed to come to equilibrium, how would the total pressure differ from that in part (a)? Explain your answer without doing a detailed calculation.

If the volume was increased, according to Le Chatlier's Principle, the equilibrium would want to shift to the side with more molecules so there would be a shift to the right with more gas particles, and with more gas particles, there would be more collisions, thus increasing pressure.

Putting it in a 3L volume box after all volume box would be like total inducing a shift by increasing volume.

- If you don't consider it a shift, then (P_total would be the same as K_p is only affected by temperature so all the calculations would be the same) but I consider the question a shift
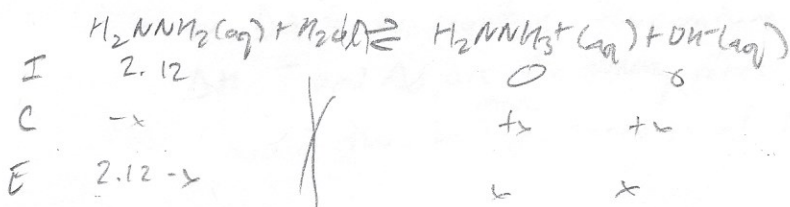
this is +t3

2) (15 pts) Hydrazine, H_2NNH_2, is an inorganic compound which is mainly used as a foaming agent in the preparation of polymer foams. It is also a weak base:

$$H_2NNH_2(aq) + H_2O \rightleftharpoons H_2NNH_3^+ (aq) + OH^- \qquad pK_b = 5.90$$
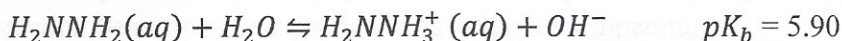
a. A solution is prepared by dissolving 68 g of hydrazine in enough water to produce 1 L of solution. Calculate the pH of the solution.

Molar Mass Hydrazine = $4(1.008) + 2(14.01) = 32.052$ g/mol

$[H_2NNH_2] = \left(\dfrac{68g}{1} \times \dfrac{1mol}{32.052g}\right) \div 1L = 2.12 M$

$$H_2NNH_2(aq) + H_2O \rightleftharpoons H_2NNH_3^+(aq) + OH^-(aq)$$

I	2.12	0	0
C	$-x$	$+x$	$+x$
E	$2.12-x$	x	x

$K_b = 10^{-pK_b} = 1.26 \times 10^{-6}$

$K_b = \dfrac{[H_2NNH_3^+][OH^-]}{[H_2NNH_2]}$

$1.26 \times 10^{-6} = \dfrac{x^2}{2.12-x}$ ← Assume x is small

$\sqrt{1.26 \times 10^{-6}(2.12)} = x$

$x = 1.63 \times 10^{-3} M$

$[OH^-] = 1.6 \times 10^{-3} M$

x should be two decimals (1.6×10^{-3})

$pOH = -\log[OH^-] = -\log(1.63 \times 10^{-3})$

$= 2.79$

Validity check: $\dfrac{1.63 \times 10^{-3}}{2.12} \times 100\% < 5\%$ ✓

$pH = 14 - pOH = 14 - 2.79 = \boxed{11.21}$ +9

b. When ammonia gas is bubbled through the hydrazine solution, the following reaction occurs:

$$H_2NNH_2 (aq) + 4 NH_3 (g) \rightarrow 3 N_2 (g) + 8 H_2 (g) \qquad \Delta H° = +89 \text{ kJ/mol}$$
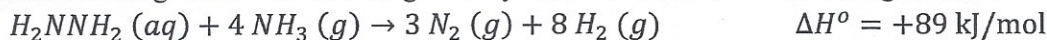
Assuming that the ammonia gas completely reacts with the hydrazine, how does the addition of a small amount of ammonia gas affect the pH of the solution? Explain your answer.
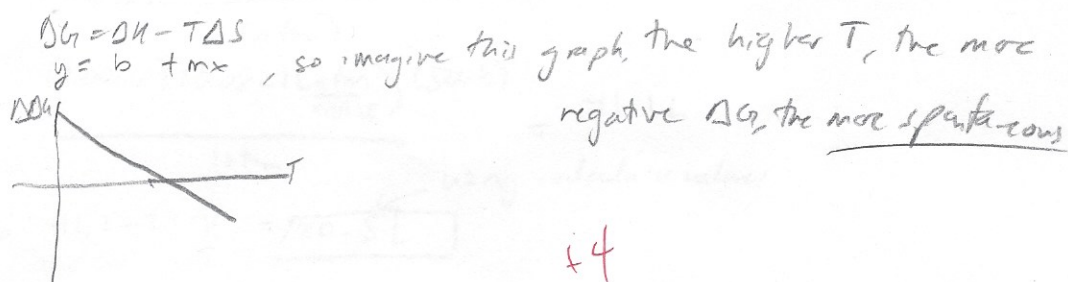
The addition of the ammonia would lead to the initial molarity of H_2NNH_2 to decrease as some of it reacted with ammonia. This would lead to a shift to the left by Le chatelier's principle to reestablish equilibrium which would decrease the concentration of $[OH^-]$ ions. This decrease in concentration would increase the pOH, and thus decrease the pH. Another way to think is that this ammonia would lower the initial concentration of H_2NNH_2 and the K_b would be the same, so with $1.26 \times 10^{-6} = \dfrac{x^2}{2.12}$, 2.12 would be smaller, making $[OH^-]$ smaller, which would thus decrease pH.

+2

c. The reaction described in part **(b)** is spontaneous at room temperature. By directly referencing the chemical reaction equation, state and explain the thermodynamic driving force(s) for this reaction. Would the reaction be more or less spontaneous at higher temperatures?

For a reaction to be spontaneous, ΔG should be zero, as seen by $\Delta G = \Delta H - T\Delta S$. ΔH of this reaction is $+89 kJ/mol$, and the ΔS is positive as the reaction proceeds from 4 moles of gas to 11 moles of gas, increasing disorder. If $\Delta G = (+) - T(+)$, then for ΔG to be negative, temperature would have to be high. ΔH, T, and ΔS are the driving forces of the reaction. The reaction would thus be more spontaneous at higher temperatures

$\Delta G = \Delta H - T\Delta S$
$y = b + mx$, so imagine this graph the higher T, the more negative ΔG, the more spontaneous

+4

3) (15 pts) Consider an ideal gas for which, in the temperature range of interest, the constant pressure heat capacity may be treated as $\frac{5}{2}R$. The temperature of 1.00 mol of this gas is raised gradually and reversibly from 250 K to 500 K in a cylinder with a moveable piston which maintains a constant external pressure of 1 atm.

$q_p = \Delta H$

a. Calculate the value of q, ΔV, w, ΔU, ΔH and ΔS for this process.

As there is constant pressure, $q_p = \Delta H = n c_p \Delta T$

$$= 1.00 mol \left(\frac{5}{2}\right)\left(\frac{8.314 J}{mol\, K}\right)(500k-250k) = 5.20 \times 10^3 J$$

$$= \boxed{5.20\ kJ}$$

$$\boxed{q_p = \Delta H}$$

$\Delta S = n c_p \ln\left(\frac{T_F}{T_i}\right)$

$$= (1.00 mol)\left(\frac{5}{2}\right)\left(\frac{8.314 J}{mol\,K}\right)\left(\ln\left(\frac{500k}{250k}\right)\right) = \boxed{14.4 J/k}$$

$V_0 = \frac{nRT_0}{P} = \dfrac{(1.00 mol)\left(0.0821\frac{Latm}{mol\,k}\right)(250k)}{(1 atm)} = 20.5\ L$

$V_F = \frac{nRT_F}{P} = \dfrac{(1.00 mol)\left(0.0821\frac{Latm}{mol\,k}\right)(500k)}{1 atm} = 41.1\ L$

using calculator values

$\Delta V = V_F - V_0 = (41.1 - 20.5)L = \boxed{20.5\ L}$

$w = -P_{ext}\Delta V = -(1 atm)(20.5 L) = -20.5\ Latm \times \dfrac{101.325 J}{1 Latm} \times \dfrac{1 kJ}{1\times10^3 J} = \boxed{-2.08\ kJ}$

$\Delta U = q + w = 5.20\ kJ - 2.08\ kJ = \boxed{3.12\ kJ}$ ✓

b. Suppose this process had been performed irreversibly (i.e. quickly heated to 500 K). Which of the variables q, ΔV, w, ΔU, ΔH, and ΔS would differ from their values in part (a)? Explain your answer(s).

skip

4) (15 pts) Benzene is an important organic chemical compound with the chemical formula C_6H_6. It is a volatile compound and exists in equilibrium with its vapor:

$$C_6H_6(l) \leftrightharpoons C_6H_6(g)$$
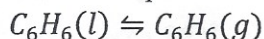
Given the following data for liquid benzene

$\Delta H_f^o = 49$ kJ/mol $\qquad\qquad \Delta G_f^o = 124.5$ kJ/mol

$\Delta H_{vap}^o = 33.9$ kJ/mol $\qquad \Delta G_{vap}^o = 5.2$ kJ/mol

Determine:

a. The enthalpy and free energy of formation of gaseous benzene.

$$\Delta h_{rxn}^o = H_f^o \, products - h_f^o \, freactants \quad , \quad \Delta H_{rxn}^o = \Delta H_{var}^o$$

$$\frac{33.9 \text{kJ}}{\text{mol}} = h_f^o C_6H_6(g) - 49 \text{kJ/mol}$$

$$\boxed{H_f^o C_6H_6(g) = 82.9 \text{kJ/mol}}$$

$$\Delta G_{rxn}^o = G_f^o \, products - \Delta G_f^o \, freactants \qquad \Delta G_{vap}^o = 5.2 \text{kJ/mol}$$

$$\frac{5.2 \text{kJ}}{\text{mol}} = G_f^o C_6H_6(g) - G_f^o C_6H_6(l)$$

$$G_f^o C_6H_6(g) = 5.2 \text{kJ/mol} + 124.5 \text{kJ/mol}$$

+3

$$\boxed{G_f^o C_6H_6(g) = 129.7 \text{kJ/mol}}$$

Assume the benzene is at the boiling point temperature already so that temperature change i wren't considered.

b. The partial pressure of benzene at equilibrium.

$$\Delta G^o = -RT \ln k$$

$$k = e^{\frac{-\Delta G^o}{RT}} = e^{-\left(\frac{5.2 \text{kJ}}{\text{mol}}\right) / \left(8.314 \frac{J}{\text{mol k}} \times \frac{1 \text{kJ}}{1\times10^3 J}\right)(298k)}$$

$T = T@STP = 25° + 273$
$= 298k$

$$k = 0.123$$

At equilibrium, K_p expression is

$$k_p = P_{C_6H_6(g)} \qquad \text{where } P_{C_6H_6(g)} \text{ is the partial pressure of benzene at equilibrium}$$

+6

$$\therefore \boxed{0.123 = P_{C_6H_6(g)} \atop atm}$$

This is the partial pressure of benzene at equilibrium

c. The entropy of vaporization of benzene under normal conditions and an estimate of the normal boiling point temperature of benzene, assuming that ΔH and ΔS are temperature independent.

Under normal conditions $\rightarrow$ STP

$$T = 298 k$$

$\Delta u = 0$ when at equilibrium, or a phase change like vaporization.

$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$

$$\not{S2kT}_{mol} = 33.9 kJ/mol - 298 \Delta S_{vap}$$

$$\Delta S_{vap} = \frac{-28.7 kJ/mol}{1} \times \frac{1 \times 10^3 J}{1 kkJ}$$

$$\frac{}{298 k}$$

$$= \boxed{96.3 \frac{J}{mol \cdot K} = \Delta S_{vap}}$$

$\Delta G = \Delta h - T\Delta S$

$0 = \Delta u_\phi - T\Delta S_\phi$

$T\Delta S_\phi > \Delta u_\phi$

$\Delta S_\phi = \frac{\Delta u_\phi}{T}$

$+6$

$$\Delta S_{vap} = \frac{\Delta H_{vap}}{T_{Boil}} \Rightarrow T_{Boil} = \frac{\Delta H_{vap}}{\Delta S_{vap}} = \frac{33.9 kJ/mol}{(96.3 \frac{J}{mol \cdot k} \times \frac{1 kJ}{1 \times 10^3 J})} =$$

$$\boxed{T_{Boil} = 352 k}$$

BONUS: Points for these questions are recorded separately and will <u>not</u> be added to your assessment grade. Points earned on bonus questions will only be considered at the end of the quarter and may be used to assist students that are on the borderline between letter grades.

1) Consider the following reactions:

$$R\ I)\ 4\ NH_3\ (g) + 3\ O_2\ (g) \rightarrow 2\ N_2\ (g) + 6\ H_2O\ (g)$$
$$R\ II)\ 4\ NH_3\ (g) + 5\ O_2\ (g) \rightarrow 4\ NO\ (g) + 6\ H_2O\ (g)$$
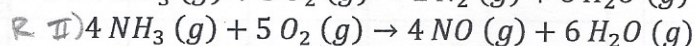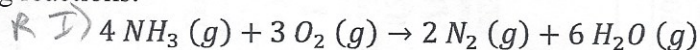
Is there a major difference in the entropy change between the two reactions? Explain your answer.

Yes, there is a major difference. For RI, N_2 has a few microstates but NO has many more microstates as N-O can be paired with $N-O_1$, NO_2, NO_3, etc. if you think of it as 4 O atoms being reused to form N-O. N_2 can only pair with one of the other $N_{>1}$, $N_{>2}$, $N_{>3}$, $N_{>4}$, etc. This means that RII has more microstates than RI as the NH_3 and H_2O microstates are the same for both reactions. Thus RII has greater $S_{products}$, and as $S_{reactants}$ of both RI and RII are similar, RII has a greater entropy change.

2

2) You have purchased a bottle of highly purified water, whose label claims to have no contaminants that would make it acidic or basic. You open the bottle and pour yourself a glass of the water. You then decide to measure its pH. Surprisingly, you find that it is slightly acidic. Why?

The bottle is open, so it's exposed to particles in the air. Naturally, certain air particles are soluble, so gas particles will dissolve in water. Let's say it's HCO_3, so $HCO_3 + H_2O \rightleftharpoons H_3O^+ + CO_3^{2-}$ for example. These air particles dissolved will slightly increase the $[H_3O^+]$ which would slightly decrease pH or make it more acidic. Another option is that the water is at a different temperature (hotter) which increases K_w and which thus decreases the $[H_3O^+]$ to something below 7. This is still technically neutral as $[H_3O^+] = [OH^-]$ but according to public idea of pH=7 being neutral, it's "acidic".

2

3) In the equation $w = -P_{ext}\Delta V$, why is there a negative sign?

Work done on a system is (+) while work done by a system is negative. If work is done on a system, the system should expand, or $\Delta V = (+)$. P_{ext} is always (+). This would be contradictory if $w = +P_{ext}\Delta V$, so there is a negative sign as a correcting factor to make it so that work done by a system is negative.

2